PATENT SPECIFICATION

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(19)

(54) POLYMERIC PHENAZINIUM COMPOUNDS

(71) We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new polymeric phenazinium compounds, a process for their manufacture and their use in acidic copper electrolytes for the deposition of glossy, self-levelling copper coatings.

It has been known for a long time that small quantities of certain organic substances may be added to acid copper electrolytes, especially to the most widely used sulphuric acid copper electrolytes, with the aim of producing glossy coatings instead of a crystalline, matt deposition. For this purpose there have been used, for example, polyethyleneglycol, thiourea and its derivatives, thiohydantoin, thiocarbamic acid esters and thiophosphoric acid esters; these compounds, however, no longer have any practical significance because the copper coatings obtained with their aid do not satisfy present-day demands. Thus, these coatings are either too brittle or they have insufficient gloss or have a relief-like aspect within certain current density ranges.

The addition of certain safranines either by themselves as proposed in German Specification No. 947,656 or in admixture with thiourea or its substitution products as proposed in German Specification No. 1,004,880 — likewise leads to copper coatings having such unsatisfactory properties.

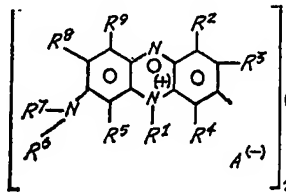
It has also been proposed to add thiourea-formaldehyde condensates (German Specifications Nos. 1,152,863 and 1,165,962) and certain compounds whose molecule contains C=S groups (German Specification No. 1,218,247).

While the copper coatings produced with the aid of these additives are glossy, they do not always satisfy the increasing demands of the industry because their self-levelling activity is not up to requirements.

It has also been proposed to add polyalkylene imines in conjuction with organic thio compounds (German Specification No. 1,246,347) and polyvinyl compounds in admixture with oxygen-containing, high-molecular compounds and organic thio compounds (German Offenlegungsschrift No. 1,521,062). Such copper electrolytes, however, do not permit the use of high cathodic current densities, and moreover the deposited copper coatings produced with such electrolytes can be nickel-coated only after a preliminary intermediate treatment.

The present invention is based on the observation that the shortcomings of the known acidic copper electrolytes discussed above are prevented by adding at least one compound of the general formula I, as defined below, to an acidic copper electrolyte. In addition, by adding at least one compound of the general formula I, as defined below, acidic copper electrolytes are improved so much that they can be used at higher current densities and in conjunction with other previously known glossing agents for the deposition of especially level copper coatings that can be nickel-plated without an intermediate treatment.

The present invention accordingly provides a compound of the general formula I



(I),

in which n represents an integer within the range of from 2 to 100, preferably from 4 to 20, A represents an acid residue, and, when n represents 2, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and R^9 are identical or different and each represents a hydrogen atom, an alkyl group containing 1 to 5 carbon atoms or an unsubstituted or substituted aryl group, and, when n is greater than 2, R^5 or R^8 in each monomeric phenazinium group represents a free valency and the remaining symbols R^1 to R^9 have the meanings given above.

The present invention also provides an acidic copper electrolyte containing a compound of the general formula I as defined above.

As alkyl groups there may be mentioned, for example, methyl and ethyl groups.

As aryl groups there may be mentioned, for example, phenyl groups which, if desired, may be substituted by, for example, methyl, ethyl, methoxy or ethoxy groups.

As acid residues there may be mentioned, for example, the residues of hydrochloric acid (Cl^-), sulphuric acid (HSO_4^-), nitric acid NO_3^-) and acetic acid (CH_3COO^-).

The amounts in which the compounds of the general formula I are to be added to the copper electrolytes to achieve a distinct improvement of the copper deposition are surprisingly very small, namely 0.0005 to 0.1 g, preferably 0.0005 to 0.03 g. per litre.

Table I below lists examples of compounds of the present invention and their preferred concentrations in acidic copper electrolytes.

It is believed that linking occurs not only via the 3-position of the phenazinium group but also via the 5- and 7-positions.

TABLE I

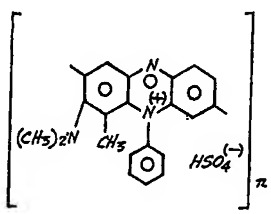
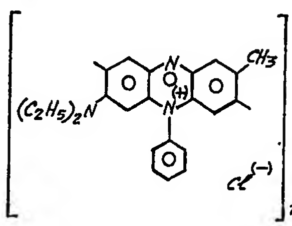
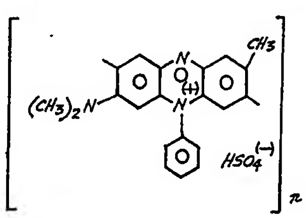
No.	Compound	n = about	Preferred concentration g/litre
1		12	0.004—0.08
2		10	0.003 — 0.03
3		19	0.001 — 0.03

TABLE I cont.

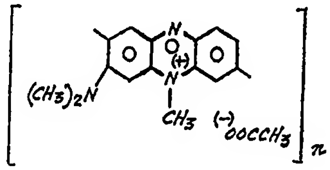
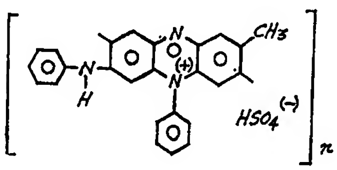
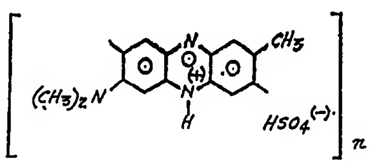
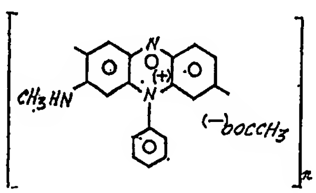
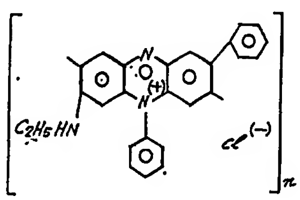
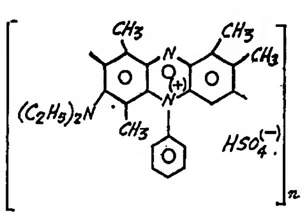
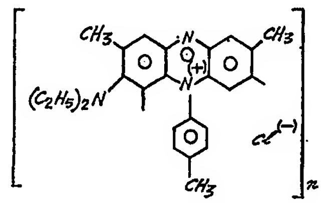
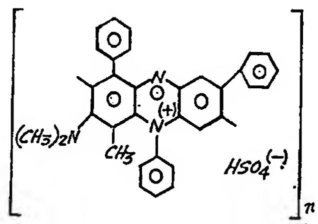
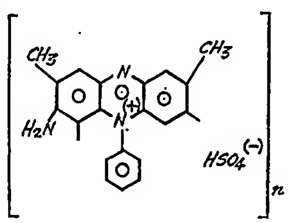
No.	Compound	$n =$ about	Preferred concentration g/litre
4		27	0.01 — 0.08
5		7	0.01 — 0.06
6		30	0.005 — 0.06
7		13	0.001 — 0.03
8		5	0.005 — 0.05
9		4	0.002 — 0.06

TABLE I cont.

No.	Compound	n = about	Preferred concentration g/litre
10		10	0.004 — 0.04
11		3	0.01 — 0.1
12		13	0.002 — 0.04

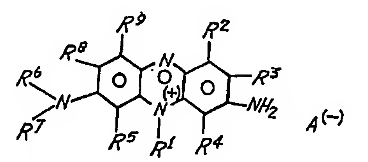
These compounds may be prepared, for example, as follows:

2 Moles of aminosulphate, for example 2-methyl - 3 - amino - 6 - dimethylamino - 9-phenyl-phenazinium sulphate, are suspended in 4.5 litres of sulphuric acid of 20% strength and during the course of 3 hours at −5°C diazotised with 650 ml of nitrosylsulphuric acid containing 2.2 moles of nitrous acid. The excess nitrous acid is decomposed with amidosulphonic acid and the reaction solution heated to 20°C, during which a strong evolution of nitrogen occurs. When nitrogen is no longer being evolved, the batch is neutralized with a base, for example a potassium hydroxide solution.

On standing the reaction product crystallizes out. After this product has been dried it can be used immediately in a suitable dilution in an acidic copper electrolyte.

Examples 1 to 12 below describe the manufacture of the compounds listed in Table I.

The present invention accordingly further provides a process for the manufacture of a compound of the general formula I, as defined above, wherein a compound of the general formula II



(II),

in which A has the meaning given above and R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and R^9 each represents a hydrogen atom, an alkyl group containing 1 to 5 carbon atoms or an unsubstituted or substituted aryl group, is diazotised in an acid solution and nitrogen is liberated from the resulting diazonium salt.

The diazotisation of the amino compounds is advantageously carried out in a sulphuric,

hydrochloric or acetic acid solution. These acids then form the afore-mentioned acid residue represented by A. A suitable diazotising agent is, for example, sodium nitrite or nitrosylsulphuric acid.

The nitrogen may be liberated from the diazonium salt by boiling the reaction solution obtained after the diazotisation. The so-called boiling of the diazonium salts formed may take place at a temperature within this range of from 5 to 100°C, preferably from 10 to 25°C.

The reaction products settle out from the acid reaction solution or can be precipitated therefrom by neutralization with a base, for example ammonia or a sodium or potassium hydroxide solution. This is followed by a conventional isolation method.

The acidic copper electrolyte of the present invention containing a compound of the general formula I is in general a sulphuric acid copper sulphate solution of the following composition:

Copper sulphate $CuSO_4 . 5H_2O$:	125—260 g per litre
Sulphuric acid H_2SO_4:	20— 85 g per litre.

Instead of copper sulphate it is possible to use at least partially other copper salts. The sulphuric acid may be replaced partially or entirely by fluoroboric acid, phosphoric and/or other acids. The electrolyte may be free from chloride — which is in most cases advantageous when requiring an improvement of the gloss and of the self-levelling of coatings produced from the electrolyte — or it may contain chlorides, for example alkali metal chlorides or hydrochloric acid in an amount ranging from 0.001 to 0.2 g per litre.

When one or several of the compounds according to the present invention of the general formula I is/are added to such copper electrolytes, the deposit obtained from the electrolytes — which is normally crystalline and matt without such an addition — is glossy within a wide range of current densities. In addition, the cathodic density may be increased by about 50% without thereby causing faults, especially blooming within the range of high current densities. To achieve a specified coating thickness it is therefore possible to shorten the time of exposure correspondingly and to achieve a greater throughput of goods in an installation of a given size.

Moreover, the compounds according to the present invention are also particularly suitable for promoting the deposition of non-cloudy and high-gloss copper coatings in conjunction with other, conventional glossing agents and/or wetting agents. An electrolyte that contains a compound listed in Table I also displays an excellent ageing behaviour. Even after a current passage of 200 to 400 Ampere hours per litre or more the resulting copper coatings are just as high-gloss, level and ductile as those produced with a fresh batch of electrolyte. No injurious decomposition products result from these compounds which would necessitate a purification operation, for example with active carbon.

A particularly distinct and sudden improvement in gloss and levelling effect is achieved by adding the compounds of the general formula I to copper electrolytes containing as glossing agents oxygen-containing, high-molecular weight compounds as well as organic thio compounds which advantageously should contain one or more than one group imparting solubility in water.

The amounts of these compounds, in grams per litre, added to the copper electrolyte are approximately within the following ranges:

Oxygen-containing, high-molecular weight compounds		0.01 — 20.0
	preferably	0.02 — 8.0
organic thio compounds, containing groups imparting solubility in water		0.0005 — 0.2
	preferably	0.01 — 0.1

The following Table II lists examples of oxygen-containing, high-molecular weight compounds and their preferred concentrations:

TABLE II

No.	Compound	Preferred concentration, g/litre
1	Polyvinyl alcohol	0.05 — 0.4
2	Carboxymethylcellulose	0.05 — 0.1
3	Polyethyleneglycol	0.1 — 5.0
4	Polypropyleneglycol	0.05 — 1.0
5	Stearic acid polyglycol ester	0.5 — 8.0
6	Oleic acid polyglycol ester	0.5 — 5.0
7	Stearyl alcohol polyglycol ether	0.5 — 8.0
8	Nonylphenol polyglycol ether	0.5 — 6.0

The following Table III lists examples of organic thio compounds containing a group imparting solubility in water and their preferred concentrations:

TABLE III

No.	Compound	preferred concentration g/litre
1	Sodium salt of N,N-diethyl-dithiocarbamic acid-(sulpho-propyl)-ester	0.01 — 0.1
2	Sodium mercaptobenzthiazole-S-propanesulphonate	0.02 — 0.1
3	Sodium 3-mercaptopropane-1-sulphonate	0.005 — 0.1
4	Bis-(3-sodium sulphopropyl)-disulphide	0.005 — 0.2
5	Disodium salt of thiophosphoric acid-O-ethyl-bis-(sulphopropyl)-ester	0.01 — 0.15
6	Trisodium salt of thiophosphoric acid-tris-(sulphopropyl)-ester	0.02 — 0.15
7	sodium isothiocyanopropylsulphonate	0.05 — 0.2
8	thioglycollic acid	0.001 — 0.003

Thus, the addition of the compounds listed in Table I to copper electrolytes that contain the known glossing agents listed in Tables II and III results in two decisive industrial advantages:

1. The permissible cathodic current density is increased by up to 50%.
2. The self-levelling effect, that is to say the reduction of rough spots in the underlying metal, is increased (for a coating 24 μm thick) from 40—50% to about 70—80%.

The concentration of the individual compounds in the copper electrolyte may be varied within wide limits. It has proved advantageous for the proportion by weight of the compounds given as examples in Tables I, II and III to be 1:10:2 to 1:200:20.

The following Examples illustrate the invention:

Example 1.

Manufacture of Compound No. 1.

I Mole of 3 - amino - 5 - methyl - 6-dimethylamino - 9 - phenylphenazinium hydrogen sulphate was suspended in 2 litres of sulphuric acid of 25% strength and during the course of 4 hours at -10°C diazotised with 300 ml of nitrosylsulphuric acid containing 1.1 mole of nitrous acid. The excess nitrous acid was decomposed with urea and the reaction solution was slowly heated to 30°C, during which a strong evolution of nitrogen occurred. When nitrogen was no longer being evolved the batch was neutralized with ammonia gas. On standing, 350 g of a polymeric blue phenylphenazinium salt crystallized out. After having been dried, this polymeric dyestuff (which had a mean molecular weight of about 5000) could be used immediately in a suitable dilution in an acidic copper electrolyte.

Example 2.

Manufacture of Compound No. 2.

1 Mole of 2 - methyl 3 - amino - 6 - diethylamino - 9 - phenyl - phenazinium chloride was suspended in 2 litres of hydrochloric acid of 30% strength and at -10°C cautiously diazotised during the course of 5 hours with a solution of 1.1 mole of sodium nitrite in 250 ml of water. The excess nitrous acid was decomposed with amidosulphonic acid and the reaction solution heated to 20°C, during which a strong current of nitrogen was evolved.

On cessation of the evolution of nitrogen the batch was neutralized with potassium hydroxide. After being allowed to stand, 300 g of the resulting blue polymeric dyestuff, having a molecular weight of 4000, were filtered off with suction.

Example 3.

Manufacture of Compound No. 3.

2 Moles of 2 - methyl - 3 - amino - 6-dimethylamino - 9 - phenyl - phenazinium sulphate were suspended in 4.5 litres of sulphuric acid of 20% strength and during the course of 3 hours at -5°C diazotised with 650 ml of nitrosylsulphuric acid containing 2.2 moles of nitrous acid. The excess nitrous acid was decomposed with amidosulphonic and the reaction solution heated to 20°C, during which a strong evolution of nitrogen occurred. On cessation of the evolution of nitrogen the batch was neutralized with a potassium hydroxide solution.

On standing, 800 g of a blue reaction product crystallized out. After having been dried, this product (which had a molecular weight of about 8000) could be used immediately in a suitable dilution in an acidic copper electrolyte.

Example 4.

Manufacture of Compound No. 4.

A suspension of 0.1 mole of 3 - amino - 6-dimethylamino - 9 - methyl - phenazinium acetate in 250 ml of glacial acetic acid was cautiously diazotised at -5°C with a solution of 0.12 mole of sodium nitrite in 50 ml of water. The excess nitrous acid was decomposed with urea and the reaction solution heated for a short time at the boil. After concentration to 100 ml and cooling, the resulting precipitated polymeric dyestuff, having a mean molecular weight of about 8000, could be filtered off with suction. Yield: 20 g.

Example 5.

Manufacture of Compound No. 5.

A suspension of 0.1 mole of 2 - methyl - 3-amino - 6 - phenylamino - 9 - phenyl - phenazinium hydrogen sulphate in 250 ml of sulphuric acid of 35% strength was diazotised at -20°C with 30 ml of nitrosylsulphuric acid containing 0.12 mole of nitrous acid. The excess nitrous acid was decomposed with amidosulphonic acid and the reaction mixture slowly heated to 50° C. On cessation of the evolution of nitrogen the batch was neutralized with a sodium hydroxide solution and the resulting polymeric dyestuff, which was contaminated with some sodium sulphate, and had a mean molecular weight of about 3000, was filtered off with suction. Yield: 15 g.

Example 6.

Manufacture of Compound No. 6.

A suspension of 0.05 mole of 2 - methyl-3 - amino - 6 - dimethyl - amino - phenazinium hydrogen sulphate in 50 ml of sulphuric acid of 40% strength was diazotised at -5°C with 15 ml of nitrosylsulphuric acid containing 0.06 mole of nitrous acid. The excess nitrous acid was decomposed with amidosulphonic acid and the acid neutralized with ammonia. After standing for a short time a blue polymeric dyestuff, having a mean molecular weight of about 10,000, could be filtered off with suction. Yield 5 g.

Example 7.

Manufacture of Compound No. 7.

A suspension of 0.05 mole of 3 - amino-6 - methylamino - 9 - phenyl - phenazinium acetate in 200 ml of glacial acetic acid was diazotised at $-10°C$ with a solution of 0.06 mole of sodium nitrite in a small quantity of water. The excess nitrous acid was decomposed with urea, and the reaction solution was heated to 40°C and then concentrated and the resulting precipitated dyestuff, having a mean molecular weight of about 5000, was filtered off with suction. Yield: 8 g.

Example 8.

Manufacture of Compound No. 8.

A suspension of 0.05 mole of 2 - phenyl-3 - amino - 6 - ethylamino - 9 - phenyl-phenazinium chloride in 400 ml of hydrochloric acid of 30% strength was diazotised during the course of 1 hour with a solution of 0.06 mole of sodium nitrite in a small quantity of water. After having decomposed the excess nitrous acid with amidosulphonic acid, the batch was heated to 30°C and on the cessation of the evolution of nitrogen substantially evaporated and the resulting precipitated dyestuff, having a mean molecular weight of about 2000, was filtered off with suction. Yield: 4 g.

Example 9.

Manufacture of Compound No. 9.

A solution of 0.05 mole of 1,2,5,8 - tetramethyl - 3 - amino - 6 - diethylamino - 9-phenyl-phenazinium hydrogen sulphate in 500 ml of sulphuric acid of 50% strength was diazotised at $-10°C$ with 15 ml of nitrosylsulphuric acid containing 0.06 mole of nitrous acid. The excess nitrous acid was decomposed with amidosulphonic acid, the diazonium salt boiled and the sulphuric acid neutralized with ammonia. The resulting precipitated dyestuff, having a mean molecular weight of about 2000, was filtered off with suction. Yield: 10 g (contaminated with ammonium sulphate).

Example 10.

Manufacture of Compound No. 10.

A suspension of 0.05 mole of 2,7 - dimethyl - 3 - amino - 6 - diethylamino - 9-tolyl-phenazinium chloride in 50 ml of hydrochloric acid of 30% strength was cautiously diazotised at $-5°C$ with a solution of 0.06 mole of sodium nitrite in a small quantity of water. The excess nitrous acid was decomposed with amidosulphonic acid, the reaction solution heated to 80°C and then extensively concentrated and the resulting precipitated dyestuff, having a mean molecular weight of about 4000, was filtered off with suction. Yield: 8 g.

Example 11.

Manufacture of Compound No. 11.

A solution of 0.05 mole of 2,8 - diphenyl-3 - amino - 5 - methyl - 6 - dimethylamino-9 - phenyl phenazinium hydrogen sulphate in 500 ml of sulphuric acid of 50% strength was diazotised at 10°C with 15 ml of nitrosylsulphuric acid containing 0.06 mole of nitrous acid. The excess nitrous acid was then decomposed with amidosulphonic acid. After boiling the diazonium compound and neutralization with ammonia, the resulting precipitated blue dyestuff, having a mean molecular weight of about 1500, was filtered off with suction. Yield: 9 g.

Example 12.

Manufacture of Compound No. 12.

A suspension of 2 moles of 2,7 - dimethyl-3,6 - diamino - 9 - phenyl - phenazinium hydrogen sulphate in 4.5 litres of sulphuric acid of 20% strength was diazotised during the course of 5 hours at $-10°C$ with 650 ml of nitrosylsulphuric acid containing 2.2 moles of nitrous acid. The excess nitrous acid was decomposed with amidosulphonic acid and the reaction solution heated to 25°C, during which a strong current of nitrogen was evolved. On cessation of the evolution of nitrogen the batch was neutralized with ammonia; the resulting polymeric red-brown dyestuff which settled out on standing and had a mean molecular weight of about 5000 was filtered off with suction. Yield: 750 g of dyestuff (contaminated with ammonium sulphate).

Example 13.

Brass sheet or previously nickel-plated steel sheet was copper-plated in an aqueous electrolyte containing

220 g/litre of copper sulphate ($CuSO_4.5H_2O$) and

50 g/litre of concentrated sulphuric acid

at an electrolyte temperature of 20 to 25°C while moving the cathode. The deposits were crystalline and matt. When the current density exceeded 4 Ampere/dm^2, there appeared in the corners of the cathode sheets pulverulent copper deposits which adhered only loosely. When 0.06 g/litre of the compound given as compound No. 1 in Table I above was added to the electrolyte, it was possible to increase the current density to a maximum of 6 Ampere/dm^2, all the other operating conditions being the same, without the aforementioned faults taking place. Furthermore, the copper coating obtained was glossy.

Example 14.

0.6 g/litre of polypropyleneglycol and
0.02 g/litre of sodium 3 - mercaptopropane-1-sulphonate

were added as glossing agents to an aqueous copper electrolyte containing

200	g/litre of copper sulphate ($CuSo_4 . 5H_2O$),
60	g/litre of concentrated sulphuric acid and
0.05	g/litre of sodium chloride.

At an electrolyte temperature of 20 to 25°C and a current density of 6.0 Ampere/dm² and while injecting air, glossy, non-cloudy copper coatings were in fact obtained but the levelling effect on rough spots in the underlying metal was only 45% at a coating thickness of 24µm. When there was added to the electrolyte 0.008 g/litre of the compound given as compound No. 3 in Table I above the levelling effect under the same operating conditions rose to 76%, that is to say it was increased by 70%.

Example 15.

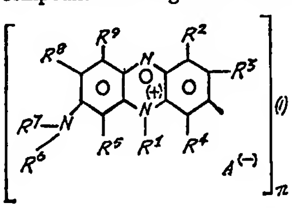
4.0	g/litre of nonylphenol polyglycol ether and
0.02	g/litre of the sodium salt of N,N-diethyl - dithiocarbamic acid - (sulphopropyl)-ester

were added to the electrolyte described at the beginning of Example 14.

At an electrolyte temperature of 20 to 25°C, a current density of 5.0 Ampere/dm², constant cathode rod movement and at a coating thickness of 24 µm of copper the levelling effect achieved was about 50%. By adding to this electrolyte 0.01 g/litre of the compound given as compound No. 6 in Table I above, the levelling effect was increased to 78%, that is to say by 56%.

WHAT WE CLAIM IS:—

1. A compound of the general formula I



in which n represents an integer within the range of from 2 to 100, A represents an acid residue, and, when n represents 2, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ each represents a hydrogen atom, an alkyl group containing 1 to 5 carbon atoms or an unsubstituted or substituted aryl group, and, when n is greater than 2, R⁵ or R⁸ in each monomeric phenazinium group represents a free valency and the remaining symbols R¹ to R⁹ have the meanings given above.

2. A compound as claimed in claim 1, wherein the alkyl group is a methyl or ethyl group.

3. A compound as claimed in claim 1 or 2, wherein the aryl group is an unsubstituted phenyl group.

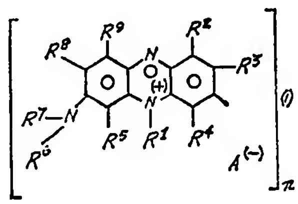
4. A compound as claimed in claim 1 or 2, wherein the aryl group is a phenyl group substituted by a methyl, ethyl, methoxy or ethoxy group.

5. A compound as claimed in any one of claims 1 to 4, wherein the acid residue is a Cl atom or a HSO_4, NO_3 or CH_3COO group.

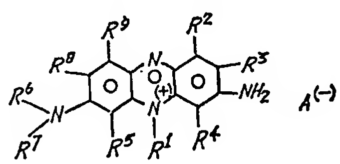
6. A compound as claimed in any one of claims 1 to 5, wherein n represents an integer within the range of from 4 to 20.

7. Any one of the compounds as claimed in claim 1 and listed in Table I herein.

8. A process for the manufacture of a compound of the general formula I



in which n represents an integer within the range of from 2 to 100, A represents an acid residue, and, when n represents 2, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ and R⁹ each represents a hydrogen atom, an alkyl group containing 1 to 5 carbon atoms or an unsubstituted or substituted aryl group, and, when n is greater than 2, R⁵ or R⁸ in each monomeric phenazinium group represents a free valency and the remaining symbols R¹ to R⁹ have the meanings given above, wherein a compound of the general formula II



(II),

in which A has the meaning given above and R¹, R², R³, R⁴, R⁵, R⁶, R⁷ R⁸ and R⁹ each represents a hydrogen atom, an alkyl group containing 1 to 5 carbon atoms or an unsubstituted or substituted aryl group, is diazotised in an acid solution and nitrogen is liberated from the resulting diazonium salt.

9. A process as claimed in claim 8, wherein the alkyl group is a methyl or ethyl group.

10. A process as claimed in claim 8 or 9, wherein the aryl group is an unsubstituted phenyl group.

11. A process as claimed in claim 8 or 9, wherein the aryl group is a phenyl group substituted by a methyl, ethyl, methoxy or ethoxy group.

12. A process as claimed in any one of claims 8 to 11, wherein n represents an integer within the range of from 4 to 20.

13. A process as claimed in any of claims 8 to 12, wherein the compound of the general formula II is diazotised with sodium nitrite or with nitrosylsulphuric acid.

14. A process as claimed in any one of claims 8 to 13, wherein the diazotisation is carried out in a sulphuric, hydrochloric or acetic acid solution.

15. A process as claimed in any one of claims 8 to 14, wherein the nitrogen is liberated from the diazonium salt by boiling the reaction solution obtained after the diazotisation.

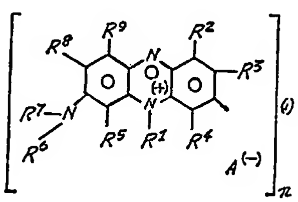
16. A process as claimed in claim 15, wherein the boiling is carried out at a temperature within the range of from 5 to 100°C.

17. A process as claimed in claim 15, wherein the boiling is carried out at a temperature within the range of from 10 to 25°C.

18. A process as claimed in claim 8, conducted substantially as described in any one of Examples 1 to 12 herein.

19. A compound of the general formula I, as defined in claim 8, whenever made by the process claimed in any one of claims 8 to 18.

20. An acidic copper electrolyte containing a compound of the general formula I



in which n represents an integer within the range of from 2 to 100, A represents an acid residue, and, when n represents 2, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and R^9 each represents a hydrogen atom, an alkyl group containing 1 to 5 carbon atoms or an unsubstituted or substituted aryl group, and, when n is greater than 2, R^5 or R^8 in each monomeric phenazinium group represents a free valency and the remaining symbols R^1 to R^9 have meanings given above.

21. An electrolyte as claimed in claim 20, wherein the alkyl group is a methyl or ethyl group.

22. An electrolyte as claimed in claim 20 or 21, wherein the aryl group is an unsubstituted phenyl group.

23. An electrolyte as claimed in claim 20 or 21, wherein the aryl group is a phenyl group substituted by a methyl, ethyl methoxy or ethoxy group.

24. An electrolyte as claimed in any one of claims 20 to 23, wherein the acid residue is a Cl atom or a HSO_4, NO_2 or CH_3COO group.

25. An electrolyte as claimed in any one of claims 20 to 24, wherein n represents an integer within the range of from 4 to 20.

26. An electrolyte as claimed in any one of claims 20 to 25, which contains two or more compounds each having the general formula I as defined in claim 20.

27. An electrolyte as claimed in any one of claims 20 to 25, which contains a single compound of the general formula I, as defined in claim 20, in an amount within the range of from 0.0005 to 0.1 g/litre.

28. An electrolyte as claimed in any one of claims 20 to 25, which contains a single compound of the general formula I, as defined in claim 20, in an amount within the range of from 0.0005 to 0.03 g/litre.

29. An electrolyte as claimed in any one of claims 20 to 26, which contains two or more compounds each having the general formula I, as defined in claim 20, in a total amount within the range of from 0.0005 to 0.1 g/litre.

30. An electrolyte as claimed in any one of claims 20 to 26, which contains two or more compounds each having the general formula I, as defined in claim 20, in a total amount within the range of from 0.0005 to 0.03 g/litre.

31. An electrolyte as claimed in any one of claims 20 to 30, which also contains an oxygen-containing, high molecular weight compound.

32. An electrolyte as claimed in claim 31, wherein the oxygen-containing, high molecular weight compound is present in an amount within the range of from 0.01 to 20.0 g/litre.

33. An electrolyte as claimed in claim 31, wherein the oxygen-containing, high molecular weight compound is present in an amount within the range of from 0.02 to 8.0 g/litre.

34. An electrolyte as claimed in any one of claims 20 to 33, which also contains an organic thio compound containing a group imparting solubility in water.

35. An electrolyte as claimed in claim 34, wherein the organic thio compound containing a group imparting solubility in water is present in an amount within the range of from 0.0005 to 0.2 g/litre.

36. An electrolyte as claimed in claim 34, wherein the organic thio compound containing a group imparting solubility in water is present in an amount within the range of from 0.01 to 0.1 g/litre.

37. An electrolyte as claimed in any one of claims 20 to 36, which contains a compound listed in Table I herein.

38. An electrolyte as claimed in any one of claims 20 to 37, which contains any one of the compounds listed in Table I herein in the corresponding concentration given in the Table.

39. An electrolyte as claimed in any one of claims 20 to 38, which contains a compound listed in Table I herein, a compound listed in Table II herein and a compound listed in Table III herein in the relative proportions

by weight within the range of from 1:10:2 to 1:200:20.

40. An electrolyte as claimed in any one of claims 20 to 39, which contains copper sulphate in an amount within the range of from 135 to 260 g/litre and sulphuric acid in an amount within the range of from 20 to 85 g/litre.

41. An electrolyte as claimed in any one of claims 20 to 40, which also contains a glossing agent not selected from compounds of the general formula I, as defined in claim 20, oxygen containing, high molecular weight compounds and organic thio compounds containing a group imparting solubility in water.

42. An electrolyte as claimed in any one of claims 20 to 41, which also contains a wetting agent.

43. Any one of the electrolytes as claimed in claim 20 and described in Examples 13 to 15 herein.

44. A process for coating a surface with copper, wherein the surface is coated by electrolytic deposition from an electrolyte as claimed in any one of claims 20 to 43.

45. A surface whenever coated by the process claimed in claim 44.

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